

08/248935

1/27	Sub
429	Class
ISSUE CLASS	

545512



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SERIAL NUMBER 08/248,935	FILING DATE 05/25/94 RULE 60	CLASS 429
SUBCLASS		GROUP ART UNIT 1102

APPLICANTS

JOHN B. BATES, OAK RIDGE, TN; NANCY J. DUDNEY, KNOXVILLE, TN.

CONTINUING DATA***
VERIFIED THIS APPLN IS A DIV OF 07/921,538 07/29/92 PAT

1378

FOREIGN/PCT APPLICATIONS***
VERIFIED

1378

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Foreign priority claimed 35 USC 118 conditions met	<input type="checkbox"/> yes <input checked="" type="checkbox"/> no	AS FILED	STATE OR COUNTRY TN	SHEETS DRWGS. 0	TOTAL CLAIMS 3	INDEP. CLAIMS 1	FILING FEE RECEIVED \$710.00
Verified and Acknowledged		Examiner's Initials					

ADDRESS

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OAK RIDGE, TN 37831-8243

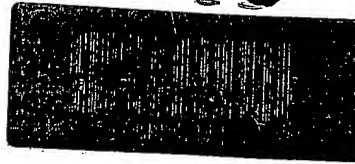
TITLE

AN ELECTRA-OPTICAL DEVICE INCLUDING A NITROGEN CONTAINING ELE

U.S. DEPT. OF COMM./PAT. & TRADEMARK OFFICE

PARTS OF APPLICATION FILED SEPARATELY		Applicat	
NOTICE OF ALLOWANCE MAILED		CLAIMS A	
5/17/95		Total Claims 3	
ISSUE FEE		DRA	
Amount Due \$1710.00	Date Paid 6/22/95	Sheets Drwg 0	
Label Area		ISSUE BATCH NUMBER J4	
KATHRYN GORGOS PRIMARY EXAMINER GROUP 1100		Primary Examiner	
PREPARED FOR ISSUE		WARNING: The information disclosed herein may be restricted. Unauthorized disclosure by the United States Code Title 35, Sections 122, 181 and 368. Patent & Trademark Office is restricted to authorized employees and	

08/ 248935



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CONTENTS

1. Application _____ papers.
2. *Pre amalta*
3. *Reg. (3)*
4. *Comm B*
5. *Examiner interview Summary*
6. *Notice of Allow*
7. *PTO ANT OCT 03 1997*
8. *Petition R-1.48(b)*
9. *Petition granted*
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SEARCHED

Class	Sub.	Date	Exmr.
359	265	11/21/94	BF See
	275		
429	192		
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	218		
	247		
	248		
204	127		
	421		
Updated		3-16-95	BF See

SEARCH NOTES

	Date	Exmr.
APS Search	11/21/94	BF See

INTERFERENCE SEARCHED

Class	Sub.	Date	Exmr.
429	192	3/13/95	BF See
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The
United
States
of
America



PTO-1584

PTO UTILITY GRANT
Paper Number 7

The Commissioner of Patents
and Trademarks

*Has received an application for a patent
for a new and useful invention. The title
and description of the invention are en-
closed. The requirements of law have
been complied with, and it has been de-
termined that a patent on the invention
shall be granted under the law.*

Therefore, this

United States Patent

*Grants to the person or persons having
title to this patent the right to exclude
others from making, using or selling the
invention throughout the United States
of America for the term of seventeen
years from the date of this patent, sub-
ject to the payment of maintenance fees
as provided by law.*

Bence Lehman

Commissioner of Patents and Trademarks

Karina J. Gager

Attest

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POSITION	ID NO.	DATE
CLASSIFIER	18	6-16-94
EXAMINER	308	6/19/94
TYPIST	21	6/20/94
VERIFIER	211	6/20/94
CORPS CORR.		
SPEC. HAND		
FILE MAINT.		
DRAFTING		

INDEX OF CLAIMS

Claim	Date
Final	Original
1	1/18/94
2	1/18/94
3	1/18/94
4	1/18/94
5	1/18/94
6	1/18/94
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SYMBOLS

- ✓ Rejected
- = Allowed
- (Through numeral) Canceled
- + Restricted
- N Non-elected
- I Interference
- A Appeal
- O Objected

STAPLE

☆ U.S. GOVERNMENT PRINTING OFFICE 1993-347-700

PATENT NUMBER

APPLICATION SERIAL NUMBER

556872/80

APPLICANT'S NAME (PLEASE PRINT)

Rule 1 a d

IF REISSUE, ORIGINAL PATENT NUMBER -

INTERNATIONAL CLASSIFICATION 6

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ISSUE CLASSIFICATION SLIP

**U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE**

Claim 1

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21/8/94

Final	
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Original

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Claim

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(REV. 2-92)U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE

SERIAL NO.

248935

GROUP/ART UNIT

1102

ATTACHMENT
TO
PAPER
NUMBER

3

NOTICE OF REFERENCES CITED

APPLICANT(S)

Bates et al

U.S. PATENT DOCUMENTS

*	DOCUMENT NO.	DATE	NAME	CLASS	SUB-CLASS	FILING DATE IF APPROPRIATE
A	5206756	4/27/93	Chestre	359	265	
B	5142406	8/25/92	Lampert et al	359	275	
C						
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FOREIGN PATENT DOCUMENTS

*	DOCUMENT NO.	DATE	COUNTRY	NAME	CLASS	SUB-CLASS	PERTINENT SHTS. DWG.	PP. SPEC.
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P								
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OTHER REFERENCES (Including Author, Title, Date, Pertinent Pages, Etc.)

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EXAMINER

DATE

Bruce Sel

11/21/94

* A copy of this reference is not being furnished with this office action.
(See Manual of Patent Examining Procedure, section 707.05 (a).)

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NEAL

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE



Division patent application of
Patent Application Serial
07/921,538 filed 29 July 1992:

John B. Bates
Nancy J. Dudney

Docket No.: 957-X-7

Examiner: S. Barts

Art Unit: 1204.

Serial No.:

Filing Date:

Title: THIN FILM BATTERY AND
METHOD FOR MAKING SAME

PRELIMINARY AMENDMENT UNDER 37 C.F.R. 1.115

Honorable Commissioner of Patents
and Trademarks
Washington, D.C. 20231

Sir:

Submitted herewith is a preliminary amendment under 37 C.F.R. 1.115 requesting that the specification and claims of the present divisional patent application be amended as follows:

In the Specification

Delete the title and substitute --An Electro-Optical Device--.

al Page 1, before the first sentence of the first paragraph, insert This application is a
division of application Serial No. 07/921,538, filed 29 July 1992, ~~presently pending~~
now U.S. Pat. No. 5,338,645.

In the Claims

Please cancel Claims 1-26 and 30.

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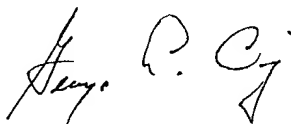
Remarks

In a telephone conversation on 19 May 1993 and a subsequent Office Action dated 28 May 1993, the Examiner issued a restriction to the filed claims of the parent application under 35 U.S.C. 121 as follows: Group I (Claims 1-7) drawn to an electrochemical cell; Group II (Claims 8-12) drawn to a method for making an electrochemical cell; Group III (Claims 13-15) drawn to an electrolyte; Group IV (Claims 16-19) drawn to a method for making an electrolyte; Group V (Claims 20-22) drawn to a cathode; Group VI (Claims 23-26) drawn to a method of making a cathode; and Group VII (Claims 27-29) drawn to an electro-optical device.

Pursuant to the restriction, Applicants elected to first prosecute, without traverse, the Claims of Group I. The Examiner issued a notice of allowance of Claims 1-5 and 30, as amended, of the original Claims 1-7 of Group I in the parent application Serial No. 07/921,538 and Applicants cancelled Claims 6 and 7.

By this Preliminary Amendment to the Divisional Application submitted herewith under 37 C.F.R. 1.60, Applicants cancel Claims 1-26 and 30. Claims now pending in the present Application are Claims 27-29.

Respectfully submitted,



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Date of Deposit: May 25, 1994

I hereby certify that the enclosed correspondence is being deposited with the U.S. Postal Service's "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Washington, D.C. 20231.

Claire M. Chitwood
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Claire M. Chitwood
(Signature of person mailing papers)

A



11X-2/28/95
041-11/28/94

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: John B. Bates
Nancy J. Dudney

Docket No.: 957X-7

Serial No.: 08/248,935

Examiner: B. Bell

Filing Date: 25 May 1994

Art Unit: 1102

Title: AN ELECTRO-OPTICAL DEVICE

AMENDMENT UNDER 37 CFR 1.115

RECEIVED

MAR 9 1995

GROUP 1100

Commissioner of Patents and Trademarks
Box Non-Fee Amendment
Washington, D.C. 20231

Sir:

This amendment is filed on behalf of the Applicants in the above-identified patent application in response to the Examiner's Office Action dated 28 November 1994, and is believed to place this application in condition for allowance.

IN THE SPECIFICATION

At page 8, after line 16, please insert the following

paragraph: --Conventional electro-optical devices known as "smart windows" are typically formed as a layered structure having a first electrode such as an anode layer, an electrochromic layer, an electrolyte or conductive layer and a second electrode such as a cathode layer, all of which are optically transparent. A limitation of such conventional electro-optical devices is that the electrolyte or conductive layer tends to be unstable and react with the electrodes. Any of

such conventional electro-optical devices may be made choice of conventional materials for the electrodes and electrochromic layers by one skilled in the art and using the novel electrolyte claimed by Applicants for the conventional electrolyte layer. The enhanced stability of Applicants' novel electrolyte arising from the inclusion of nitrogen provides for electro-optical devices having enhanced performance over conventional devices.--

REMARKS

The Examiner rejects Claims 27-29 under 35 USC 112 for failure to provide an enabling description of the claimed invention. The Examiner, however, also states that Claims 27-29 are allowable over the prior art of record and that Claims 27-29 would be allowable if rewritten or amended to overcome the 35 USC 112 rejection.

In a telephone conversation with the Examiner on 28 February 1995, the Examiner concurred that inclusion of the above paragraph in the specification clarified that Applicants' novel electrolyte had utility and novelty both as to electrochemical cells and to electro-optical devices where, in the latter case, all known conventional materials could be chosen by one skilled in the art for the electrode and electrochromic layers and the novel electrolyte of Applicants' claimed invention could be substituted for the conventional electrolyte layer. Therefore, no amendment of Claims 27-29 was deemed necessary and the aforementioned paragraph would be effective to overcome the 35 USC 112 rejection.

The Claims as originally filed are thus deemed distinguishable

over the cited prior art and the application is considered in condition for allowance. Consideration of the present application in view of the foregoing comments is requested, and a favorable action is earnestly solicited.

Respectfully submitted,

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I hereby certify that this correspondence is being deposited with the U.S. Postal Service as First-Class Mail in an envelope addressed to Commissioner of Patents and Trademarks, Washington, D.C. 20231, on 28 February, 1995 by *George L. Craig*.

George L. Craig

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ABSTRACT OF THE DISCLOSURE

Described is a thin-film battery, especially a thin-film microbattery, and a method for making same having application as a backup or primary integrated power source for electronic devices. The battery includes a novel electrolyte which is electrochemically stable and does not react with the lithium anode and a novel vanadium oxide cathode. Configured as a microbattery, the battery can be fabricated directly onto a semiconductor chip, onto the semiconductor die or onto any portion of the chip carrier. The battery can be fabricated to any specified size or shape to meet the requirements of a particular application. The battery is fabricated of solid state materials and is capable of operation between -15°C and 150°C .

THIN FILM BATTERY AND METHOD FOR MAKING SAME

This invention was made with Government support under Contract No. DE-AC05-84OR21400 awarded by the U.S. Department of Energy to Martin Marietta Energy Systems, Inc. The Government has certain rights in this invention.

BACKGROUND OF INVENTIONField of Invention

The invention is directed to a thin-film battery and a method for making same. More particularly, the invention is directed to a new thin-film lithium battery having a novel electrolyte permitting a battery to be fabricated having greatly enhanced energy density and specific energy over conventionally available batteries. The invention is also directed to a novel cathode permitting a battery to be fabricated having significantly enhanced energy densities over conventionally available batteries.

Ins. 81

Description of Prior Art

A battery is one of two kinds of electrochemical devices that convert the energy released in a chemical reaction directly into electrical energy. In a battery, the reactants are stored close together within the battery itself, whereas in a fuel cell the reactants are stored externally. The attractiveness of batteries as an efficient source of power is that the conversion of chemical energy to electrical energy is potentially 100% efficient although the loss due to internal resistance is a major limiting factor. This potential efficiency is considerably greater than the conversion of thermal energy to mechanical energy as used in internal combustion engines, which always results in heat transfer losses. Moreover, the additional disadvantages of contaminants emitted into the atmosphere as byproducts of incomplete combustion and dwindling availability of fuel supplies have

intensified research into batteries as an alternative source of energy.

One limitation of conventional batteries is that they use toxic materials such as lead, cadmium, mercury and various acid electrolytes that are facing strict regulation or outright banning as manufacturing materials. Another limitation is that the amount of energy stored and/or delivered by the battery is generally directly related to its size and weight. At one end of the development spectrum, automobile batteries produce large amounts of current but have such low energy densities and specific energies due to their size and weight and such relatively lengthy recharge times that their usage as a source of propulsion is impractical. At the other end of the development spectrum, small, light, lithium batteries used to power small electronic appliances and semiconductor devices have much higher energy densities and specific energies but have not had the capability to be scaled up to provide the high energy for high power applications such as use in automobiles. Further, these small, light, lithium batteries have low charge-discharge cycle capability, limited rechargeability and, even where scaled down for microelectronics applications, size that frequently is many times larger than the semiconductor chip on which they are used.

Thin-film battery technology is foreseen as having several advantages over conventional battery technology in that battery cell components can be prepared as thin, e.g. 1 micron, sheets built up in layers using techniques common to the electronics industry according to the desired application. The area of the sheets can be varied from sizes achievable with present lithographic techniques to a few square meters providing a wide range in battery capacity. Deposition of thin films places the anode close to the cathode resulting in high current density, high cell efficiency and a great reduction in the amount of reactants

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used. This is because the transport of ions is easier and faster in thin film layers since the distance the ions must move is lessened.

Most critical to battery performance is the choice of electrolyte. It is known that the principle limitation on rechargeability of prior batteries is failure of the electrolyte. Battery failure after a number of charge-discharge cycles and the loss of charge on standing is caused by reaction between the anode and the electrolyte, e.g. attack of the lithium anode on the lithium electrolyte in lithium batteries. An extra process step of coating the anode with a protective material adds to the complexity, size and cost of the battery.

The power and energy density of a battery is also dependent upon the nature of the cathode. To achieve optimum performance, the open circuit voltage and current density on discharge should be as high as possible, the recharge rate should be high and the battery should be able to withstand many charge-discharge cycles with no degradation of performance. The vanadium oxide cathode of the present invention has a much higher capacity per mole than the crystalline TiS_2 of prior art cathodes.

The present invention avoids the limitations of present battery design and provides a novel battery having application as a battery used with manufacture of semiconductor components and as a high energy, high current macrobattery with appropriate scale-up of the described processes. The present invention includes a novel electrolyte having a good conductivity but more importantly it has electrochemical stability at high cell potentials and requires no protective layer between it and the anode during battery fabrication or use. The present invention also includes a novel cathode having a microstructure providing excellent charge/discharge properties.

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SUMMARY OF THE INVENTION

A primary object of invention is to provide a new thin-film battery and a method for making same.

5 A second object of invention is to provide a new electrolyte for a thin-film battery in which the electrolyte has good ionic conductivity and is not reactive with the battery anode.

Another object of invention is to provide a method for making an improved electrolyte for a thin-film battery.

10 A yet further object of invention is to provide a new cathode having improved microstructure for a thin-film battery and a method for making same.

These and other objects are achieved by depositing a pair of current collecting films on a substrate; depositing
15 an amorphous cathode layer on the larger of the two collecting films; depositing an amorphous lithium phosphorus oxynitride electrolyte layer over the cathode; and depositing a metallic anode layer over the electrolyte.

BRIEF DESCRIPTION OF THE DRAWING

20 Figure 1 is a schematic diagram of a thin-film battery deposited onto a semiconductor chip package with current leads extending to a semiconductor chip.

Figures 2A-2D illustrates the layers in plan view to form a thin-film battery according to the present
25 invention.

Figure 3 schematically illustrates a cross-sectional view of a thin-film battery made according to the present invention.

Figure 4A is a micrograph of a vanadium oxide cathode formed by a sputtering process where the target is aged due to prior sputtering and the process gas flow rate is less
30 than about 15 sccm.

Figure 4B is a micrograph of a vanadium oxide cathode formed by a sputtering process where the target is fresh
35 and the process gas flow rate is greater than about 15 sccm.

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Figure 5 illustrates the charge-discharge performance for a microbattery made according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

There are many possible uses for a thin-film, rechargeable battery as a primary or standby power source for low current electronic devices. A thin-film cell could be fabricated directly onto the semiconductor chip, the chip package or the chip carrier and could be fabricated to any specified size or shape to meet the requirements of a particular application. Referring to Figure 1, a possible application is shown in which a thin-film cell 10 is deposited onto a semiconductor chip package 12 with current leads 14 extending to the chip 16. A Li-VO_x cell about 8 microns thick occupying an area of 1 square centimeter as shown has a capacity of 130 microAmp-hours and could supply a current of up to 100 microAmps at a voltage ranging from 3.7 volts at full charge to about 1.5 volts near the end of its discharge. If a larger battery were deposited over the unused area of the package, the capacity and current density of the battery could of course be increased.

With reference to Figures 2A-D, the steps in fabricating such a single cell are shown. Two current collectors, vanadium for example, are deposited as a larger and a smaller 0.5 micron thick film, 18 and 20 respectively, on a substrate 22 such as glass, alumina, sapphire or various semiconductor or polymer materials. The films may be deposited by rf or dc magnetron sputtering or diode sputtering of vanadium in Argon, vacuum evaporation or other such film deposition techniques common to the semiconductor electronics industry. Similarly, an amorphous vanadium-oxide, VO_x, cathode 24 is deposited as a 1 micron thick film over the larger current collector 18 by sputtering vanadium in Argon + 14%O₂. An amorphous oxynitride lithium electrolyte film 26 is then deposited over the cathode 24 by sputtering of Li₃PO₄, lithium

orthophosphate, in 20 milliTorr of N_2 and a total gas flow of 14 sccm. As before, various film deposition techniques may be used for fabrication of the vitreous electrolyte film 26 although reactive DC sputtering is not available when lithium orthophosphate is the target as it is an insulator material and would accumulate charge until the deposition process stopped. Example targets for the described microbattery measured 25 millimeters in diameter by 3 millimeters thick and were prepared by cold pressing lithium orthophosphate powder followed by sintering of the pressed disc in air at 900°C. Deposition of a 1 micron thick film was carried out over a period of 16-21 hours at an average rate of 8-10 Angstroms per minute. The film 26 has the composition $Li_xPO_yN_z$ where x has the approximate value of 2.8; $2y + 3z$ has the approximate value of 7.8; and z has the approximate value of 0.16 to 0.46. Deposition of a film 28 of lithium over the vitreous electrolyte film 26, the intervening substrate 22 and the smaller current collector 20 completes the cell. A typical film thickness for the lithium film 28 is about 5 microns. Figure 3 is a schematic cross-section view of Figure 2D.

Example performance characteristics of such a battery as described above are an open circuit voltage of 3.6 to 3.8 volts and, for a 1 micron thick cathode, a capacity of about 130 microAmp-hours per square centimeter for a discharge to 1.5 volts. The battery is capable of producing a discharge current of up to 2 milliAmps per square centimeter and can be recharged at a current of at least 20 microAmps per square centimeter. The battery has been subjected to more than 100 charge/discharge cycles with no degradation in performance and, after the first few cycles, the efficiency of the charge/discharge process was approximately 100%. Further, the vitreous oxynitride lithium electrolyte 26 has demonstrated long-term stability in contact with the lithium anode 28 such that the battery does not require the extra protective film, typically

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lithium iodide, to prevent reaction of the lithium anode with the electrolyte.

Performance of thin-film batteries has been critically limited by the properties of the chosen electrolyte. For rechargeable lithium batteries, the electrolyte should have a high lithium ion conductivity and it must be chemically stable in contact with lithium. Films deposited by sputtering or evaporation of inorganic compounds onto substrates held at ambient temperatures are usually amorphous. This is advantageous because, for many lithium compounds, the lithium ion conductivity of the amorphous phase is orders of magnitude higher than that of the crystalline phase and the conductance of the amorphous film is often adequate for use as an electrolyte. As many of these amorphous materials have acceptable low electronic conductivities, there is a wide choice of materials available for possible application in thin-film cells which meet the first two requirements. However, instability in contact with lithium eliminates many materials from consideration and has limited development of a thin-film lithium cell. The amorphous lithium phosphorus oxynitride film 26 of the present invention is made by sputtering Li_3PO_4 in pure N_2 and has both the desired electrical properties and the stability in contact with lithium for fabrication of electrochemical cells.

A comparison of the conductivities at 25°C for several electrolyte compositions in the lithium phosphosilicate system achieved by sputtering lithium silicates and lithium phosphates in Ar and Ar + O_2 is shown in Table 1. The lithium phosphosilicate listed had the highest conductivity of the films in the $\text{Li}_2\text{O}:\text{SiO}_2:\text{P}_2\text{O}_5$ system. Several of the more highly conductive lithium phosphosilicate films with different compositions were investigated as the electrolyte for lithium cells. In each case, the lithium anode reacted with the electrolyte film 26. However, the electrolyte of the present invention was found to be stable

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in contact with the lithium anode although it contained only about 2 to 6 at.% nitrogen. Moreover, as shown in Table 1, the conductivity is more than 30 times greater than that of the film deposited by sputtering Li_3PO_4 in 40% O_2 in Argon. Incorporation of nitrogen into the thin films of the present invention increases conductivity at least five times greater than similarly prepared films containing no nitrogen. The increase in conductivity is due to an increase in lithium ion mobility rather than an increase in the number of charge carriers brought about by a change in the structure of the electrolyte. Further, such cells appear to be stable indefinitely, exhibiting only a small voltage loss which is considered to occur due to the electronic conductivity of the electrolyte.

Table 1. Comparison of amorphous lithium phosphate, phosphosilicate, and phosphorus oxynitride electrolyte films.

Target	Process Gas	Film Composition	$\sigma(25^\circ\text{C}) \times 10^8$ (S/cm)	E_g (eV)
Li_3PO_4	40 % O_2 in Ar	$\text{Li}_{2.7}\text{PO}_{3.9}$	7	0.68
$\text{Li}_3\text{PO}_4 + \text{Li}_4\text{SiO}_4$	"	$\text{Li}_{4.4}\text{Si}_{0.23}\text{PO}_{5.2}$	20	0.57
Li_3PO_4	N_2	$\text{Li}_{3.3}\text{PO}_{3.8}\text{N}_{0.22}$	240	0.56

The enhanced conductivity, superior mechanical properties of nitrided glass (e.g. hardness, resistance to fracture) and chemical stability of the oxynitride lithium electrolyte of the present invention could also be used to fabricate enhanced electro-optic devices using electrochromic layers, i.e. so called smart windows, because of the increased resistance to attack from water vapor.

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The performance of the lithium microbattery of the present invention is also very dependent on formation of the cathode. Consideration of the microstructure of the cathode is equally as important as consideration of the composition. Typical of prior thin-film batteries is the use cathodes having a characteristic crystalline microstructure. The microstructure is dependent on substrate temperature, extent of the erosion of the target material due to prior sputtering and the pressure and composition of the process gas during deposition. At substrate temperatures of 400°C, vanadium oxide cathodes, for example, consist of crystalline platelets standing on edge while films deposited onto substrates at about 50°C consist of clusters of crystalline fibrous bundles. With reference to Figure 4, two distinct types of microstructure are shown for vanadium oxide films deposited by reactive sputtering of vanadium. When deposited from an eroded target, the cathode films 28 were characterized by a high density of micron-sized fibrous clusters in Figure 4A of crystalline V_2O_5 . When a fresh target surface is used and the flow rate is increased to about 20 sccm, the microstructure of the cathode 28 has the smooth microstructure shown in Figure 4B. The advantage achieved with the amorphous structure over the crystalline structure is that at least three times more lithium ions can be inserted into cathode 28 having such amorphous structure, thus resulting in a lithium cell of much higher capacity.

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As the sputtering target, e.g. vanadium, ages, the microstructure of the films deposited with higher flow rates gradually evolves to that of the films having fibrous clusters characteristic of deposition at the lower flow rates. This change in the films is evident by a decrease in sputtered target voltage (at constant power) and as much as a 30% decrease in deposition rate.

Lithium cells fabricated with crystalline or amorphous vanadium oxide cathodes had open circuit voltages of 3.6 to 3.7 volts. However, compared with amorphous cathodes, the rates of discharge and charge that the cells with the crystalline cathodes could sustain without excessive polarization are significantly lower, usually less than 3 microAmps per square centimeter. This probably results from poor transport across the interface between the electrolyte 26 and the cathode 28 since the electrolyte 26 does not conformably coat the fibrous clusters of the crystalline cathode 28 but rather covers just the top portion, resulting in a relatively small contact area.

Lithium cells made according to the present invention having the lithium phosphorus oxynitride electrolyte 26 and the smooth amorphous cathode 28 may be discharged at rates of up to 3 milliAmps per square centimeter. With reference to Figure 5, a set of charge-discharge curves for one cycle of such a cell is shown. The total charge passed through this cell between 3.64 volts and 1.5 volts is about 575 milliCoulombs. The capacity of the cell over this voltage

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range is 130 microAmp-hours per square centimeter with an energy density of 1.2×10^6 Joules per kilogram based on combined masses of the cathode, electrolyte and anode.

The greatly enhanced energy density achievable with
5 thin-film batteries made according to the present invention may, with suitable scaling of process parameters, permit fabrication of high energy thin-film macrobatteries. For example, according to the present teachings, a 25-kWh thin-film lithium battery could be constructed by connecting in
10 series approximately 46 large-area thin-film cells. Such a battery would have an average voltage of 165 volts, a weight of 67 kilograms, a volume of 36 liters, a specific energy of 370 Watt-hours per kilogram and an energy density of 690 Watt-hours per liter.

15 While there has been shown and described what is at present considered the preferred embodiment of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as
20 defined by the appended claims.

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What is claimed is:

1. A thin-film electrochemical cell comprising:
 - a) a substrate;
 - b) a first and a second electrically conductive film deposited on the surface of said substrate, said first and
5 second films separated horizontally and said first film larger than said second film;
 - c) a third film of electrically conductive material deposited over said first film;
 - d) a fourth film of an electrolyte having nitrogen
10 contained therein deposited on and overlapping said third film to extend upon said first film and to partially extend upon said substrate separating said first and second films;
and
 - e) a fifth film of electrically conductive material
15 deposited over the remainder of said substrate separating said first and second films and over substantially all of said second and said fourth films.
2. The cell of Claim 1 wherein the substrate material is selected from the group consisting of glass, alumina, semiconductor material and polymer material.
3. The cell of Claim 1 wherein the substrate is selected from the group consisting of a semiconductor chip, a semiconductor package and a semiconductor chip carrier.

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c) operating the sputtering apparatus such that the flow rate of the process gas is at least 15 sccm under an operating pressure of about 20 milliTorrr; and

10 d) depositing said cathode as an amorphous metal-oxide film at a rate of about 2 nanometers per minute.

24. The method of Claim 23 wherein said amorphous metal oxide film is vanadium oxide.

25. The method of Claim 23 wherein said sputtering apparatus is selected from the group consisting of a reactive dc magnetron sputterer, an rf magnetron sputterer and a diode sputterer.

26. The method of Claim 23 wherein said gas mixture is 14% O₂ in Argon.

27. An electro-optical device comprising:

a) an optically transparent anode of a first electrically conductive material;

5 b) an optically transparent electrochromic material overlaying said anode;

c) an optically transparent electrolyte containing nitrogen therein overlaying said electrochromic material; and

10 d) an optically transparent cathode overlaying said electrolyte.

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